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(54)【発明の名称】 排気ガス浄化用触媒

(57)【要約】

【目的】 900℃以上でも触媒活性を有し、かつNO_xに対する高い浄化能力を有する三元触媒を得る。

【構成】 一般式 $L_{n-1-x}A_xMO_3$ (L_n はCeを除く希土類金属、AはCe又はアルカリ土類金属、Mは遷移金属で、いずれも1種又は2種以上、 $0 < x < 1$)で示されるペロブスカイト型構造の複合酸化物と、Ce及びZr、又はさらにCe以外の希土類金属を含む、少なくとも一部が複合酸化物又は固溶体となっている耐熱性酸化物と、貴金属とを共存させる。耐熱性酸化物の共存により耐熱性が高まり、貴金属の共存によりNO_xに対する浄化能力が高まる。

【特許請求の範囲】

【請求項1】 一般式 $L_{n-1-x}A_xMO_3$ (L_n はCeを除く希土類金属、AはCe又はアルカリ土類金属、Mは遷移金属で、いずれも1種又は2種以上、 $0 < x < 1$)で示されるペロブスカイト型構造の複合酸化物と、Ce及びZr、又はさらにCe以外の希土類金属を含む、少なくとも一部が複合酸化物又は固溶体となっている耐熱性酸化物と、貴金属とを共存させた排気ガス浄化用触媒。

【請求項2】 前記耐熱性酸化物はCeの100原子に対してZrが5~100原子、Ce以外の希土類金属が0~100原子の原子比となるように構成されている請求項1に記載の排気ガス浄化用触媒。

【請求項3】 貴金属は白金族である請求項1に記載の排気ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は900℃以上でも用いられる一酸化炭素(CO)、炭化水素(HC)及び酸化窒素(NO_x)の浄化能力に優れた排気ガス浄化用三元触媒に関するものである。

【0002】

【従来の技術】希土類金属、アルカリ土類金属及び遷移金属から構成されるペロブスカイト型構造を有する複合酸化物は、CO、HC及び NO_x を浄化する安価な排気ガス浄化用三元触媒として実用化が期待されている(特開昭59-87046号公報、特開昭60-82138号公報参照)。しかし、これらの触媒はいずれも800℃以下で使用するのを目的としており、自動車排ガス用触媒のように900℃以上の高温域において高い触媒活性を必要とし、かつ高温での耐久性も満足する必要がある場合には、十分な触媒とはいえない。すなわち、ペロブスカイト型構造を有する複合酸化物は、900℃以上の高温で使用すると焼結して有効表面積が減少し、触媒活性が著しく低下する。また、このペロブスカイト型複合酸化物はCO、HCの浄化能力は優れているが、 NO_x の浄化能力がやや劣っており、自動車排ガス用の三元触媒として実用に供するには十分でない。

【0003】そこで、ペロブスカイト型構造を有する複合酸化物を触媒成分として900℃以上の高温で長時間用いた場合の問題点である焼結による活性低下を防ぎ、触媒成分の NO_x 浄化能力の改善を図るために、ペロブスカイト型構造の複合酸化物と、耐熱性を有する複合酸化物と、貴金属とを共存させた排気ガス浄化用触媒が提案されている(特開平1-168343号公報参照)。そこで使用されている耐熱性複合酸化物は、触媒成分のペロブスカイト型複合酸化物と化学的性質の類似した構造を有し、希土類金属とアルカリ土類金属を有している。

【0004】

【発明が解決しようとする課題】本発明は上記引用の特開平1-168343号公報の発明と同様に、ペロブスカイト型構造の複合酸化物触媒の900℃以上での触媒活性の低下を防ぐとともに、 NO_x 浄化能力を改善することにより、その引用発明とは耐熱性酸化物の構造の異なるものを提供することを目的とするものである。

【0005】

【課題を解決するための手段】本発明は、一般式 $L_{n-1-x}A_xMO_3$ (L_n はCeを除く希土類金属、AはCe又はアルカリ土類金属、Mは遷移金属、 $0 < x < 1$)で示されるペロブスカイト型構造の複合酸化物と、Ce及びZr、又はさらにCe以外の希土類金属を含む、少なくとも一部が複合酸化物又は固溶体となっている耐熱性酸化物と、貴金属とを共存させた排気ガス浄化用触媒である。ここで、 L_n 、A及びMは1種ずつの場合に限らず、2種以上を含んでいる場合も含む。

【0006】本発明の第1の特徴は、ペロブスカイト型構造の複合酸化物からなる触媒成分に耐熱性酸化物を共存させた点にある。耐熱性酸化物はセリウム酸化物とジルコニウム酸化物、又はさらにセリウム以外の希土類金属の酸化物を含み、それらの酸化物の少なくとも一部は複合酸化物又は固溶体として存在し、900℃以上の高温においても焼結を抑制することができる。この耐熱性酸化物による効果は、触媒成分を耐熱性酸化物上に担持して用いる場合、及び触媒成分粉末と耐熱性酸化物粉末とを混合して使用する場合のいずれの場合にも有効に発揮され、900℃以上の高温で長時間使用した後でも触媒成分は担体上に高分散状態に維持されているか、又は耐熱性酸化物粉末間に高分散の状態で存在している。この耐熱性酸化物が900℃以上の高温においても熱的に安定で、触媒成分と反応しにくいので、触媒成分のペロブスカイト構造の破壊による触媒活性の低下が防がれる。

【0007】本発明の第2の特徴は、触媒成分としてのペロブスカイト型複合酸化物以外にパラジウムなどの貴金属を添加した点にある。ペロブスカイト型構造の複合酸化物それ自体は三元触媒として使用できるが、 NO_x に対する浄化能力がHC、COに比べてやや劣っている。そこで、 NO_x に対する活性を高めるために少量の貴金属を添加した。貴金属はペロブスカイト型構造の複合酸化物及び耐熱性酸化物上に担持されている。担持された貴金属は反応するペロブスカイト型複合酸化物上では固溶及び析出現象が起こり、一方、反応しない高比表面積の耐熱性酸化物上では析出状態で高分散に担持されることにより、排気ガス変動雰囲気下における900℃以上の高温でも貴金属の焼結が起きにくく、浄化活性が高度に維持される。このように、本発明にかかる触媒は、900℃以上の高温でも耐久性のある安価な排気ガス浄化用三元触媒である。

【0008】本発明のかかる触媒に用いる触媒成分の1

つであるペロブスカイト型構造の複合酸化物は、一般式 $L_{n-1-x}A_xMO_3$ である。この複合酸化物の量は触媒全量の1~80重量%が望ましい。1重量%より少ない場合は触媒活性が低く、逆に80重量%より多くなると耐熱性酸化物の効果が現われにくくなり好ましくない。この触媒成分の複合酸化物の形状、粒度、純度、比表面積などは触媒成分として通常用いられる状態であればよい。

【0009】耐熱性酸化物は触媒成分の担体として広く用いられている Al_2O_3 などと同様の状態（形状、粒度、純度、比表面積）で用いられたい。例えば、比表面積は触媒成分を高分散状態に保持するため、 $20\text{ m}^2/\text{g}$ 以上が望ましい。耐熱性酸化物中のCe、Zr、希土類金属の比率は特に制限されないが、Ceの100原子に対してZrは5~100原子、好ましくは5~50原子、Ce以外の希土類金属は0~100原子、好ましくは5~30原子の原子比となるように構成する。

【0010】他の触媒成分である貴金属は白金族のRu、Rh、Pd、Os、Ir及びPtのうちから選ばれた1種又は2種以上を用いる。これらの貴金属のうちPdを用いた場合にNO_x浄化特性が最も向上する。貴金属の量は触媒全量に対し0.01~5重量%、望ましくは0.1~2重量%がよい。貴金属が0.01重量%より少ない場合はNO_x浄化能力の向上が不十分であり、逆に5重量%を越えてもNO_x浄化能力が飽和する。これら貴金属は従来の三元触媒において通常用いられている状態（形状、粒度、純度、比表面積）で用いる。

【0011】本発明にかかる触媒は通常、触媒を製造するために行なわれている方法によって製造することができる。次に、製造方法の一例を示す。触媒成分を担体に担持した状態に製造する場合には、まず担体となる耐熱性酸化物の複合酸化物又は固溶体を、セリウム塩とジルコニウム塩又はさらに希土類金属塩を含む水溶液を600℃以上の温度で熱分解し、焼成することによって得るか、又は市販のセリア粉末（ $100\text{ m}^2/\text{g}$ 以上）にジルコニウム塩又はさらに希土類金属塩を所定の化学量論比で混合した水溶液を加え、約100℃で5~12時間大気中で乾燥し、その後600℃で3時間大気中で焼成して得る。その耐熱性酸化物からなる担体粉末に、触媒成分であるペロブスカイト型構造を有する複合酸化物を構成する金属の硝酸塩を所定の化学量論比で混合した水溶液を加え、約100℃で5~12時間大気中で乾燥し、その後さらに700~800℃で3~10時間大気中で焼成する。この熱処理により硝酸塩が熱分解し、担体粉末上にペロブスカイト型構造の複合酸化物が担持される。

【0012】次に、上記の如く耐熱性複合酸化物担体に担持したペロブスカイト型構造の複合酸化物上に、Pt、Pd、Rhなどの貴金属を担持する。例えば硝酸パラジウムの水溶液を上記粉末に含浸させ、約100℃で

5~12時間大気中で乾燥し、その後600℃で3時間大気中で焼成し、Pdを担持する。また、ペロブスカイト型構造を有する複合酸化物の微粉末と耐熱性複合酸化物の微粉末を混合した後、貴金属を担持してもよい。ペロブスカイト型構造の複合酸化物の微粉末の製造は、まずそれを構成する各金属の硝酸塩、シュウ酸塩などを混合した水溶液に、所定量の炭酸ナトリウム、炭酸アンモニウムなどの中和剤を加えて共沈させる。次にこの混合物を水洗し、濾過し、乾燥し、500~600℃で3~5時間大気中で焼成した後、粉碎し、さらに700~800℃で3~5時間大気中で焼成し、微粉末とする。この粉末の比表面積は少なくとも $10\text{ m}^2/\text{g}$ 以上であることが望ましい。このように製造したペロブスカイト型構造の複合酸化物微粉末に耐熱性酸化物粉末を混合し、さらにこの混合粉末に貴金属を上記したと同様の方法で担持し、目的とする触媒とする。

【0013】この触媒はこれにバインダーを添加し、所定の形状に成形して用いたり、又は水を加えスラリー状として基材に塗布して用いることもできる。また、基材に耐熱性酸化物を被覆した後、触媒成分であるペロブスカイト型構造の複合酸化物及び貴金属を担持して用いることもできる。

【0014】

【実施例】

（実施例1）担体として用いる耐熱性複合酸化物は市販の高比表面積の酸化セリウム粉末（CeO₂、比表面積 $130\text{ m}^2/\text{g}$ 、純度99.9%、TREO（全希土類酸化物）111.9gを用意し、これにオキシ硝酸ジルコニウム（ZrO(NO₃)₂）水溶液（液比重1.51、液中にZrO₂換算で25.0重量%含まれる）147.9g、及び硝酸イットリウム（Y(NO₃)₃）水溶液（液比重1.62、液中にY₂O₃換算で21.7重量%含まれる）26.0gを加え、よく攪拌して混合しながら110℃で10時間大気中で乾燥した。その後、大気中で600℃で3時間焼成を行ない、(Ce_{0.9}, Zr_{0.1}, Y_{0.1})O₃複合酸化物を約150g得た。

【0015】次に、この粉末を50g用意し、これに硝酸ランタン（La(NO₃)₃・6H₂O）70.4g、硝酸セリウム（Ce(NO₃)₃・6H₂O）17.7g及び硝酸コバルト（Co(NO₃)₂・6H₂O）59.2gを溶解した水溶液100mlを加えた後、110℃で10時間大気中で乾燥した。その後、大気中で800℃、3時間焼成を行ない、上記硝酸塩を熱分解し、(Ce_{0.9}, Zr_{0.1}, Y_{0.1}, Co_{0.1})O₃上にCoを含有するペロブスカイト型構造を有する複合酸化物（La_{0.9}Ce_{0.1}）CoO₃を担持した粉末を得た。

【0016】その後、この粉末に硝酸パラジウム水溶液を含浸させ、110℃で10時間大気中で乾燥し、さらに大気中で600℃で3時間の焼成を行なって、Pdを0.5g担持した触媒を（試料No. 1）を調製した。

この触媒の成分は重量比で $(La_{0.8}Ce_{0.2})CoO_3 : (Ce_{0.8}Zr_{0.2}Y_{0.2})O_2 : Pd = 50 : 50 : 0.5$ であった。

【0017】(実施例2) 実施例1で調製した $(Ce_{0.8}Zr_{0.2}Y_{0.2})O_2$ 粉末50gを用意し、これに担持されるペロブスカイト型構造の複合酸化物を得るための金属塩の添加量を、硝酸ランタン70.4g、硝酸セリウム17.7g、硝酸コバルト23.7g及び硝酸鉄 $(Fe(NO_3)_3 \cdot 9H_2O)$ 49.6gとする他は、実施例1と同様の操作により、この実施例2にかかる触媒 (試料No. 2) を調製した。この触媒の成分は重量比で $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3 : (Ce_{0.8}Zr_{0.2}Y_{0.2})O_2 : Pd = 50 : 50 : 0.5$ であった。

【0018】(実施例3) 実施例1で用いた酸化セリウム粉末132.6gにオキシ硝酸ジルコニウム水溶液98.6g及び硝酸イットリウム水溶液15.7gを加え、実施例1と同様の操作により $(Ce_{0.77}Zr_{0.20}Y_{0.03})O_2$ 耐熱性複合酸化物を得た。次に、この粉末を50g用意し、これに実施例2と同様の配合比と操作により、この実施例3にかかる触媒 (試料No. 3) を調製した。この触媒の成分は重量比で $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3 : (Ce_{0.77}Zr_{0.20}Y_{0.03})O_2 : Pd = 50 : 50 : 0.5$ であった。

【0019】(実施例4) 実施例3で調製した $(Ce_{0.77}Zr_{0.20}Y_{0.03})O_2$ 耐熱性複合酸化物粉末50gを用意し、これに硝酸ランタン79.2g、硝酸セリウム8.9g、硝酸コバルト23.7g、硝酸鉄49.6gを溶解した水溶液を加え、実施例1と同様の乾燥と焼成を行ない、 $(CeZrY)O_2$ 上に $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ を担持した粉体を得た。その後、その粉末にジニトロジアミン白金 $((NH_2)_2(NO_2)_2Pt)$ 硝酸水溶液を含浸させ、実施例1と同様の操作により、この実施例4にかかる触媒 (試料No. 4) を調製した。この触媒の成分は重量比で $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3 : (Ce_{0.77}Zr_{0.20}Y_{0.03})O_2 : Pt = 50 : 50 : 0.5$ であった。

【0020】(実施例5) 実施例1で用いた硝酸セリウム粉末111.9gにオキシ硝酸ジルコニウム水溶液147.9g及び硝酸ランタン $(La(NO_3)_3 \cdot 6H_2O)$ 22.1gを溶解した水溶液50mlを加え、実施例1と同様の操作にて $(Ce_{0.8}Zr_{0.2}La_{0.8})O_2$ 耐熱性複合酸化物を得た。次に、この粉末を50g用意し、これに担持されるペロブスカイト型構造の複合酸化物を得るための金属塩の添加量を、硝酸ランタン74.1g、硝酸ストロンチウム $(Sr(NO_3)_2)$ 9.1g、硝酸コバルト31.1g、硝酸鉄43.2gとする他は実施例1と同様の操作により、この実施例5にかかる触媒 (試料No. 5) を調製した。この触媒の成分は重量比で $(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3 : (Ce_{0.8}Zr_{0.2}La_{0.8})O_2 : Pd = 50 : 50 : 0.5$ であった。

$r_{0.8}La_{0.2})O_2 : Pd = 50 : 50 : 0.5$ であった。

【0021】(実施例6) ペロブスカイト型構造の複合酸化物 $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ 粉末の調製法を説明する。硝酸ランタン103.9g、硝酸セリウム26.1g、硝酸コバルト34.9g、硝酸鉄72.7gを純水に溶解した水溶液0.3リットルを用意した。次に、中和共沈剤として炭酸ナトリウム50gを溶解した水溶液0.5リットルを用意した。中和共沈剤を先の水溶液に滴下し、共沈物を得た。その共沈物を十分水洗し、濾過した後、真空乾燥した。これを600℃で3時間大気中で焼成後、粉碎し、その後、800℃で3時間大気中で焼成を行ない、さらに粉碎し、 $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ の粉末を作成した。実施例1で調製した $(Ce_{0.8}Zr_{0.2}Y_{0.2})O_2$ 粉末80gと上記により作成した $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ 粉末20gを十分混合した。次に、この混合粉末に硝酸パラジウム水溶液を用いてパラジウムを含浸した後、110℃で10時間乾燥し、次いで600℃で3時間大気中で焼成してPdを0.5g担持した触媒 (試料No. 6) を調製した。

【0022】(実施例7) 実施例6のペロブスカイト型複合酸化物の調製法に代えて、硝酸ランタン76.7g、硝酸ネオジウム $(Nd(NO_3)_3 \cdot 6H_2O)$ 38.2g、硝酸コバルト43.7g、硝酸鉄60.6gを用いて同様の操作にて $(La_{0.8}Nd_{0.2}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ の粉末を作成した。この粉末80gと実施例1で調製した $(Ce_{0.8}Zr_{0.2}Y_{0.2})O_2$ 粉末20gを十分混合した後、実施例6と同様にしてPdを0.5g担持した触媒 (試料No. 7) を調製した。

【0023】(実施例8) 実施例1で用いた酸化セリウム粉末137.70gにオキシ硝酸ジルコニウム98.6gを加え、実施例1と同様の操作により $(Ce_{0.8}Zr_{0.2})O_2$ 耐熱複合酸化物粉末を得た。この耐熱複合酸化物粉末50gを実施例6による $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ ペロブスカイト型粉末50gを十分混合した後、Pdを0.5g担持して触媒 (試料No. 8) を調製した。

【0024】(実施例9) 実施例6による $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ 粉末80gと実施例8による $(Ce_{0.8}Zr_{0.2})O_2$ 耐熱複合酸化物粉末20gを十分混合した後、Pdを0.5g担持して触媒 (試料No. 9) を調製した。

【0025】(実施例10) 実施例6の硝酸セリウムに代えて硝酸ストロンチウム12.7gを用いて同様の操作により $(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$ ペロブスカイト型粉末を作成した。この粉末80gと実施例8による $(Ce_{0.8}Zr_{0.2})O_2$ 耐熱複合酸化物粉末20gを十分混合した後、Pdを0.5g担持して触媒 (試料No. 10) を調製した。

【0027】(比較例1)実施例6で作成したペロブスカイト型構造の複合酸化物($\text{La}_{0.8}\text{Ce}_{0.2}$)($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3 粉末100gを用い、これに硝酸パラジウム水溶液を用いて実施例1と同様の方法でPdを0.5g担持して比較用の触媒(試料No. C1)を調製した。

【0028】(比較例2)実施例1で調製した耐熱性複合酸化物に代えて、市販の高比表面積の酸化セリウム粉末を50g用意し、これに実施例1と同様の操作で CeO_2 上に($\text{La}_{0.8}\text{Ce}_{0.2}$) CoO_3 を担持し、さらにPdを0.5g担持して比較用の触媒(試料No. C2)を調製した。この触媒の成分は重量比で($\text{La}_{0.8}\text{Ce}_{0.2}$) CoO_3 : CeO_2 :Pd=50:50:0.5であった。

【0029】(比較例3)実施例1の($\text{Ce}_{0.8}\text{Zr}_{0.2}\text{Y}_{0.2}$) O_2 を市販の $\gamma\text{-Al}_2\text{O}_3$ (比表面積110 m^2/g)に代える他、同様の操作によりこの比較例3による触媒(試料No. C3)を調製した。

【0030】(比較例4)実施例6で作成したペロブスカイト型構造の複合酸化物($\text{La}_{0.8}\text{Ce}_{0.2}$)($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3 粉末50gと市販の SrZrO_3 粉末50gとを十分に混合した後、Pdを0.5g担持した触媒*

* (試料No. C4)を調製した。

【0031】(試験例)実施例、比較例で調製した触媒について、入口ガス温度930℃の排気ガス中で5時間の浄化活性の耐久試験を行なった。ガス組成は一酸化炭素(CO)1.0%、プロピレン(C_3H_6)0.1%、二酸化炭素(CO_2)10%、水(H_2O)4%で、酸素(O_2)を変動条件とし、残部が窒素(N_2)である。

【0032】(評価)上記の耐熱・耐久試験を行なった触媒について、450℃における一酸化炭素、プロピレン及び酸化窒素の浄化率を測定した。測定に際し粉末状触媒を加圧成形し、直径が約2mmのペレット状とし、反応管に充填した。測定時の空間速度は30000/時間であり、ガス組成はCOが0.7%、 C_3H_6 が0.15%、 CO_2 が10%、 H_2O が10%、 H_2 が0.23%、NOが0.15%、 O_2 を変動条件とし、残部が N_2 である。第1表に結果を触媒の成分とともに記載した。本実施例の触媒は比較例の触媒に比べ耐久性に優れている。

【0033】

【表1】

試料 No.	触媒組成 (重量比)	浄化率		
		CO	C_3H_6	NO
1	$\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ 50+(CeZrY) O_2 50+Pd0.5	85	83	85
2	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 50+(CeZrY) O_2 50+Pd0.5	93	86	92
3	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 50+(CeZrY) O_2 50+Pd0.5	91	85	86
4	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 50+(CeZrY) O_2 50+Pt0.5	89	81	80
5	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$ 50+(CeZrLa) O_2 50+Pd0.5	93	85	87
6	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 20+(CeZrY) O_2 80+Pd0.5	86	84	84
7	$\text{La}_{0.5}\text{Nd}_{0.5}\text{Ce}_{0.12}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$ 80+(CeZrY) O_2 20+Pd0.5	87	84	85
8	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 50+(CeZrY) O_2 50+Pd0.5	85	82	83
9	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 80+(CeZrY) O_2 20+Pd0.5	88	80	87
10	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 80+(CeZrY) O_2 20+Pd0.5	86	80	85
C1	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 100+Pd0.5	82	70	68
C2	$\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ 50+ CeO_2 50+Pd0.5	73	68	61
C3	$\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ 50+ $\gamma\text{-Al}_2\text{O}_3$ 50+Pd0.5	61	57	55
C4	$\text{La}_{0.8}\text{Ce}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$ 50+ SrZrO_3 50+Pd0.5	85	80	80

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(54) **Exhaust gas purifying catalyst and method of preparing the same.**

(57) In order to obtain a three way catalyst having catalytic activity also at a temperature exceeding 900° C as well as high purification ability with respect to NO_x, a perovskite compound oxide which is expressed in a general formula Ln_{1-x}A_xMO₃, where Ln represents one or at least two rare earth metals excluding Ce, A represents Ce or one or at least two alkaline earth metals, M represents one or at least two transition metals and 0 < x < 1, a heat resistant oxide containing Ce and Zr, or further containing a rare earth metal excluding Ce so that the same is at least partially in the form of a compound oxide or a solid solution, and a precious metal are coexistently mixed with each other. Heat resistance is improved by coexistence of the heat resistant oxide, while purification ability with respect to NO_x is improved by coexistence of the precious metal.

In order to obtain an exhaust gas purifying catalyst which exhibits sufficient purification activity also at a low exhaust gas temperature condition, a double structure is attained by a core of a perovskite compound oxide such as (La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O₃ and an outer perovskite compound oxide, in which a precious metal is solidly dissolved, enclosing the core. When the precious metal is provided in excess, the excessive part thereof is dispersed in a fine particle state as a metal or an oxide.

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BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to an exhaust gas purifying catalyst which has excellent ability to convert carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxide (NOx) into CO₂, H₂O and N₂ respectively. More particularly, it relates to a three way catalyst for purifying exhaust gas which can excellently purify carbon monoxide, hydrocarbon and nitrogen oxide even if the same is used at a temperature exceeding 900 °C, an exhaust gas purifying catalyst which exhibits purification activity also at a low exhaust gas
10 temperature condition such as idling of an automobile gasoline engine or the like, and a method of preparing the same.

Description of the Background Art

15 As to a three way catalyst for purifying exhaust gas, a precious metal catalyst, which is prepared from an alumina support supporting a precious metal such as Pt, Rh or Pd, is put into practice for wide use.

On the other hand, a compound oxide having a perovskite structure, which is formed of a rare earth metal, an alkaline earth metal and a transition metal, is expected for practical use as a low-priced three way catalyst for purifying exhaust gas which can purify CO, HC and NOx (refer to Japanese Patent Laying-Open
20 Gazettes Nos. 59-87046 (1984) and 60-82138 (1985)). However, such a catalyst is suitable for use at a temperature of not more than 800 °C, and cannot sufficiently cope with automotive exhaust gas which requires high catalytic activity in a high temperature range exceeding 900 °C as well as high temperature durability. Such a perovskite compound oxide is sintered when the same is used at a high temperature exceeding 900 °C, and hence its effective surface area is reduced to cause extreme reduction of catalytic
25 activity. Further, the perovskite compound oxide is not sufficiently applicable to a three way catalyst for automotive exhaust gas due to inferiority in purification of NOx, although the same is excellent in purification of CO and HC.

In order to prevent reduction of activity caused by sintering when a compound oxide having a perovskite structure is used as a catalytic component at a high temperature exceeding 900 °C for a long
30 time thereby improving its ability to purify NOx, there has been proposed an exhaust gas purifying catalyst which is obtained by coexistently mixing a perovskite compound oxide, a heat resistant compound oxide and a precious metal with each other (refer to Japanese Patent Laying-Open Gazette No. 1-168343 (1989)). The heat resistant compound oxide which is employed therein is similar in chemical property to the perovskite compound oxide serving as a catalytic component, and contains a rare earth metal and an
35 alkaline earth metal.

In this catalyst, a precious metal such as Pd is carried on the surface of the fine perovskite compound oxide in a dispersed state.

SUMMARY OF THE INVENTION

40 In order to prevent a compound oxide catalyst having a perovskite structure from reduction of catalytic activity at a temperature exceeding 900 °C as well as to improve its ability to purify NOx similarly to the aforementioned invention disclosed in Japanese Patent Laying-Open Gazette No. 1-168343, a first object of the present invention is to provide a catalyst containing a heat resistant oxide which is different in structure
45 from that of the said invention.

The aforementioned conventional catalyst exhibits only insufficient purification activity at a low exhaust gas temperature condition in idling of an automobile or the like. With severe regulation of exhaust gas, awaited is a catalyst which exhibits sufficient purification activity at such a low exhaust gas temperature condition.

50 A second object of the present invention is to provide an exhaust gas purifying catalyst which exhibits sufficient purification activity at a low exhaust gas temperature condition.

A third object of the present invention is to provide a method of preparing the same.

In order to attain the aforementioned first object, an exhaust gas purifying catalyst according to the first invention is prepared by coexistently mixing a perovskite compound oxide which is expressed in a general
55 formula $Ln_{1-x}AxMO_3$, where Ln represents one or at least two rare earth metals excluding Ce, A represents Ce or one or at least two alkaline earth metals, M represents one or at least two transition metals and $0 < x < 1$, a heat resistant oxide containing Ce and Zr or further containing a rare earth metal excluding Ce, which is at least partially in the form of a compound oxide or a solid solution, and a precious metal.

In order to attain the aforementioned second object, an exhaust gas purifying catalyst according to the second invention at least contains an oxide having a core of a perovskite compound oxide which is expressed in a general formula $\text{Ln}_{1-x}\text{BxMO}_3$, where Ln represents one or at least two rare earth metals excluding Ce, B represents one or at least two alkaline earth metals excluding Sr or Ce, M represents one or at least two transition metals and $0 < x < 1$, and a perovskite compound oxide, in which a precious metal is solidly dissolved, enclosing core. An excessive (insoluble) part of the precious metal is dispersed in a particulate state as a metal or an oxide. In order to improve purification activity of this catalyst at a high temperature, further contained is a heat resistant oxide, containing Ce and Zr, or further containing a rare earth metal excluding Ce, which is at least partially in the form of a compound oxide and/or a solid solution, or a heat resistant oxide, which is composed of Ce. In this case, powder of the perovskite compound oxide and that of the heat resistant oxide serve as cores, to be enclosed by the perovskite compound oxide in which the precious metal is solidly dissolved.

The heat resistant oxide is preferably prepared from a compound oxide which is expressed in a general formula $(\text{CeZrLn})\text{O}_2$, where Ln represents a rare earth metal excluding Ce, such as CeO_2 , $(\text{CeZr})\text{O}_2$, $(\text{CeZrY})\text{O}_2$, $(\text{CeZrLa})\text{O}_2$ or $(\text{CeZrNd})\text{O}_2$. $(\text{CeZr})\text{O}_2$ is superior to CeO_2 in an effect of improving purification activity at a high temperature, while $(\text{CeZrLn})\text{O}_2$ is more preferable since the same is further superior in the effect of improving purification activity at a high temperature.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing three way purification activity levels of Example 12 and Comparative Example e;
 Fig. 2 is a photograph showing a section of a catalyst according to Example 14;
 Fig. 3 is an enlarged photograph showing the section of the catalyst according to Example 14; and
 Fig. 4 is a further enlarged photograph showing the section of the catalyst according to Example 14.

DETAILED DESCRIPTION OF THE INVENTION

A first feature of the first invention resides in a point that a catalytic component made of a perovskite compound oxide is coexistently mixed with a heat resistant oxide. The heat resistant oxide contains a cerium oxide and a zirconium oxide, or further contains an oxide of a rare earth metal excluding cerium, such that these oxides at least partially exist in the form of compound oxides or solid solutions, to be capable of suppressing sintering also at a high temperature exceeding 900°C . Such an effect of the heat resistant oxide is so availably provided when the catalytic component is carried on the heat resistant oxide or powder of the catalytic component is mixed with that of the heat resistant component, that the catalytic component is still maintained on the support in a highly dispersed state or exists between particles of the heat resistant oxide in highly dispersed states also after the catalyst is used at a high temperature exceeding 900°C for a long time. Since the heat resistant oxide is thermally stable and hardly reactive with the catalytic component also at a high temperature exceeding 900°C , it is possible to prevent reduction of catalytic activity which may be caused by breakage of the perovskite structure of the catalytic component.

A second feature of the first invention resides in a point that a precious metal such as palladium is added to a perovskite compound oxide serving as a catalytic component. While a compound oxide having a perovskite structure itself can be used as a three way catalyst, its purification ability with respect to NO_x is slightly inferior as compared with those for HC and CO. Therefore, a small amount of a precious metal is added in order to improve activity with respect to NO_x . Such a precious metal is carried on the perovskite compound oxide and a heat resistant oxide. The as-carried precious metal causes solid solution and precipitation on the reactive perovskite compound oxide, while the same is carried in a precipitated state in high dispersion on the unreactive heat resistant oxide having a high specific surface area. Thus, the precious metal is hardly sintered even at a high temperature exceeding 900°C at an exhaust gas fluctuation atmosphere, to keep highly purification activity at a high degree.

Thus, the first invention provides a three way catalyst for purifying exhaust gas, which is durable also at a high temperature exceeding 900°C , at a low cost.

The perovskite compound oxide forming the catalytic component of the catalyst according to the first invention is expressed in a general formula $\text{Ln}_{1-x}\text{AxMO}_3$. The total catalyst preferably contains 1 to 80 percent by weight of this composite oxide. If the content is less than 1 percent by weight, catalytic activity is unpreferably reduced, while no sufficient effect of the heat resistant oxide is attained if the content exceeds

80 percent by weight. The compound oxide may have arbitrary shape, grain size, purity, specific surface area and the like in ordinary ranges for serving as a catalytic component.

The heat resistant oxide may be employed in states of shape, grain size, purity and specific surface area similar to those of a widely used support such as Al_2O_3 . For example, the heat resistant oxide preferably has a specific surface area of at least $20 \text{ m}^2/\text{g}$, in order to maintain the catalytic component in a highly dispersed state. While the ratios of Ce, Zr and the rare earth metal contained in the heat resistant oxide are not particularly restricted, a preferable atomic ratio of Zr to Ce is 5/100 to 100/100, more preferably 5/100 to 50/100, and that of the rare earth metal excluding Ce to Ce is 0/100 to 100/100, more preferably 5/100 to 30/100.

The precious metal serving as another catalytic component is prepared from one or at least two metals selected from the platinum group of Ru, Rh, Pd, Os, Ir and Pt. When Pd is selected from these precious metals, an NO_x purifying activity is most improved. The total catalyst preferably contains 0.01 to 5 percent by weight, more preferably 0.1 to 2 percent by weight of the precious metal. If the content is less than 0.01 percent by weight, the NO_x purifying ability is insufficiently improved, while the NO_x purifying ability is saturated if the content exceeds 5 percent by weight. Such a precious metal is employed in arbitrary shape, grain size, purity and specific surface area in ordinary ranges for serving as a component of a three way catalyst.

The catalyst according to the first invention can be prepared by a method which is generally carried out for preparing a catalyst. An exemplary preparation method is now described.

In order to prepare a catalyst comprising a catalytic component which is carried on a support, a compound oxide or a solid solution of a heat resistant oxide for serving as the support is first obtained by thermally decomposing an aqueous solution containing a cerium salt and a zirconium salt or further containing a rare earth metal salt at a temperature exceeding 600°C and firing the same, or adding an aqueous solution, which is mixed with a zirconium salt or further mixed with a rare earth metal salt at a prescribed stoichiometric ratio, to commercially available ceria powder of at least $100 \text{ m}^2/\text{g}$, drying the mixture in the air at about 100°C for 5 to 12 hours and thereafter firing the mixture in the air at 600°C for 3 hours. An aqueous solution, which is mixed with nitrates of metals forming a perovskite compound oxide serving as a catalytic component at a prescribed stoichiometric ratio, is added to the as-formed support powder of the heat resistant oxide, so that the mixture is dried in the air at about 100°C for 5 to 12 hours and thereafter further fired in the air at 550 to 800°C for 3 to 10 hours. The nitrate is thermally decomposed by this heat treatment, so that the perovskite compound oxide is carried on the support powder.

Then, a precious metal such as Pt, Pd or Rh is carried on the perovskite compound oxide which is carried on the heat resistant compound oxide support in the aforementioned manner. The aforementioned powder is impregnated with an aqueous solution of palladium nitrate, for example, dried in the air at about 100°C for 5 to 12 hours, and thereafter fired in the air at 600°C for 3 hours, to carry Pd.

Alternatively, fine powder of the perovskite compound oxide and that of the heat resistant compound oxide may be mixed with each other to thereafter carry the precious metal. In order to prepare such fine powder of the perovskite compound oxide, a prescribed amount of a neutralizer such as sodium carbonate or ammonium carbonate is added to an aqueous solution which is mixed with nitrates or oxalates of metals forming the perovskite compound oxide and coprecipitated. Then the mixture is washed, filtered, dried, fired in the air at 500 to 600°C for 3 to 5 hours, thereafter pulverized, and further fired in the air at 550 to 800°C for 3 to 5 hours, to prepare fine powder. This powder preferably has a specific surface area of at least several m^2/g , for example, more than $5 \text{ m}^2/\text{g}$. The as-formed fine powder of the perovskite compound oxide is mixed with powder of a heat resistant oxide to carry a precious metal in a method similar to the above, thereby obtaining the target catalyst.

A binder can be added to the catalyst for formation into a prescribed shape, or water can be added thereto for preparation of slurry, which is applied to a support substrate. Alternatively, a base material can be covered with the heat resistant oxide, to carry the perovskite compound oxide and the precious metal serving as catalytic components.

The feature of the second invention resides in a double structure formed by a core of a perovskite compound oxide containing no precious metal and another perovskite compound oxide containing a precious metal which is dispersed around the core. The precious metal or a precious metal oxide solidly dissolved in the outer perovskite compound oxide layer or carried on the surface of the inner perovskite compound oxide serving as the core mutually influences with the perovskite compound oxides, to contribute to purification.

The precious metal is prepared from one or at least two metals selected from a group of Pd, Pt, Ru, Rh and Ir. Pd is particularly preferable since the same improves low temperature purification activity and NO_x purification activity.

A method of preparing the catalyst according to the second invention comprises steps of making 100 parts by weight of the aforementioned perovskite compound oxide or a mixture of the aforementioned perovskite compound oxide and a heat resistant oxide impregnated with and/or adsorb the precious metal through a precious metal salt solution containing 0.2 to 5.0 parts by weight of a precious metal in total
 5 conversion and being adjusted to be not more than pH 4, drying the as-formed mixture and thereafter firing the same at a temperature of 250 to 800 °C. When the perovskite compound oxide is dipped in the precious metal salt solution which is adjusted to be not more than pH 4, elements contained in a crystal are partially eluded and a plurality of salts containing the precious metal are bonded onto the periphery of a core of remaining perovskite compound oxide powder and heat resistant oxide powder which are not eluded. This
 10 mixture is dried at 130 °C for 24 hours, for example, and thereafter fired in the air at a temperature exceeding 250 °C, preferably at 500 to 800 °C for 3 hours, for example, to form a perovskite compound oxide crystal in which the precious metal is solidly dissolved around the core, thereby attaining a double structure of the oxide. An excessive part of the precious metal, which has been insoluble in the recrystallized perovskite compound oxide crystal, is dispersed in a metal state or in the form of a precious
 15 metal oxide.

A water soluble precious metal salt is preferably prepared by chloride such as PdCl_2 , PtCl_2 or $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, nitrate such as $\text{Pd}(\text{NO}_3)_2$, $\text{Ru}(\text{NO}_3)_3$ or $\text{Rh}(\text{NO}_3)_3$, or a dinitrodiamine salt such as $\text{Pd}(\text{NO}_2)_2 \cdot (\text{NH}_3)_2$ or $\text{Pt}(\text{NO}_2)_2(\text{NH}_2)_2$, whose aqueous solution exhibits a strong acid property.

The catalyst according to the second invention exhibits excellent purification activity with respect to HC, CO and NOx also at a low exhaust gas temperature of 100 to 200 °C in idling or the like.
 20 When a heat resistant oxide is contained, the catalyst exhibits excellent durability also at a high temperature exceeding 900 °C.

The preparation method according to the present invention is adapted to dissolve and recrystallize the perovskite compound oxide by a simple method of controlling the pH of the solution of the precious metal to be carried in the perovskite compound oxide or a mixture of the perovskite compound oxide and the heat resistant oxide, so that the precious metal can be solidly dissolved in its crystal for providing excellent exhaust gas purification activity.
 25

Examples of First Invention

Example 1

A heat resistant compound oxide for serving as a support was prepared from 111.9 g of commercially available cerium oxide (CeO_2) powder having a high specific surface area with a specific surface area of
 35 130 m^2/g and purity of 99.9 %/TREO (total rare earth oxide), and 147.9 g of an aqueous solution of oxy zirconium nitrate ($\text{ZrO}(\text{NO}_3)_2$), having liquid specific gravity of 1.51 and containing 25.0 percent by weight of $\text{ZrO}(\text{NO}_3)_2$ in ZrO_2 conversion, and 26.0 g of an aqueous solution of yttrium nitrate ($\text{Y}(\text{NO}_3)_3$), having liquid specific gravity of 1.62 and containing 21.7 percent by weight of $\text{Y}(\text{NO}_3)_3$ in Y_2O_3 conversion, were added to the heat resistant compound oxide, stirred and mixed with each other, so that the as-obtained mixture
 40 was dried in the air at 110 °C for 10 hours. Thereafter the mixture was fired in the atmosphere at 600 °C for 3 hours, to obtain about 150 g of a $(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2$ compound oxide.

Then, 50 g of this powder was mixed with 100 ml of an aqueous solution, in which 70.4 g of lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), 17.7 g of cerium nitrate ($\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 59.2 g of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved, and the mixture was dried in the air at 110 °C for 10 hours. Thereafter the mixture
 45 was fired in the air at 800 °C for 3 hours to thermally decompose the nitrate components, thereby obtaining powder carrying a perovskite compound oxide ($\text{La}_{0.8}\text{Ce}_{0.2}$) CoO_3 containing Co on $(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2$.

Thereafter this powder was impregnated with an aqueous solution of palladium nitrate, dried in the air at 110 °C for 10 hours, and further fired in the air at 600 °C for 3 hours, to prepare a catalyst (sample No. 1) carrying 0.5 g of Pd. This catalyst was composed of $(\text{La}_{0.8}\text{Ce}_{0.2})\text{CoO}_3 : (\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2 : \text{Pd} = 50:50:0.5$ in
 50 weight ratios.

Example 2

A catalyst (sample No. 2) according to Example 2 was prepared in a similar manner to Example 1 by
 55 employing 50 g of the aforementioned $(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2$ powder, except for that 70.4 g of lanthanum nitrate, 17.7 g of cerium nitrate, 23.7 g of cobalt nitrate and 49.6 g of iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were added thereto. This catalyst was composed of $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3 : (\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2 : \text{Pd} = 50:50:0.5$ in weight ratios.

Example 3

98.6 g of an aqueous solution of oxy zirconium nitrate and 15.7 g of an aqueous solution of yttrium nitrate were added to 132.6 g of the cerium oxide powder employed in Example 1, to obtain a heat resistant compound oxide of $(\text{Ce}_{0.77}\text{Zr}_{0.20}\text{Y}_{0.03})\text{O}_2$ in a similar manner to Example 1.

Then, 50 g of this powder was employed to prepare a catalyst (sample No. 3) according to Example 3, with blending ratios similar to those of Example 2 in a similar manner thereto. This catalyst was composed of $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3 : (\text{Ce}_{0.77}\text{Zr}_{0.20}\text{Y}_{0.03})\text{O}_2 : \text{Pd} = 50:50:0.5$ in weight ratios.

Example 4

An aqueous solution, in which 79.2 g of lanthanum nitrate, 8.9 g of cerium nitrate, 23.7 g of cobalt nitrate and 49.6 g of iron nitrate were dissolved, was added to 50 g of the heat resistant compound oxide powder of $(\text{Ce}_{0.77}\text{Zr}_{0.20}\text{Y}_{0.03})\text{O}_2$ prepared in Example 3, and the mixture was dried and fired in a similar manner to Example 1, to obtain powder carrying $(\text{La}_{0.9}\text{Ce}_{0.1})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ on $(\text{CeZrY})\text{O}_2$.

Thereafter this powder was impregnated with a nitrate solution of dinitrodiamine platinum $((\text{NH}_3)_2(\text{NO}_2)_2\text{Pt})$, to prepare a catalyst (sample No. 4) according to Example 4 in a similar manner to Example 1. This catalyst was composed of $(\text{La}_{0.9}\text{Ce}_{0.1})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3 : (\text{Ce}_{0.77}\text{Zr}_{0.20}\text{Y}_{0.03})\text{O}_2 : \text{Pt} = 50:50:0.5$ in weight ratios.

Example 5

50 ml of an aqueous solution, in which 147.9 g of an aqueous solution of oxy zirconium nitrate and 22.1 g of lanthanum nitrate $(\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$ were dissolved, was added to 111.9 g of the cerium nitrate powder employed in Example 1, to obtain a heat resistant compound oxide of $(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{La}_{0.05})\text{O}_2$ in a similar manner to Example 1.

Then, 50 g of this powder was employed to prepare a catalyst (sample No. 5) according to Example 5 in a similar manner to Example 1, except for that 74.1 g of lanthanum nitrate, 9.1 g of strontium nitrate $(\text{Sr}(\text{NO}_3)_2)$, 31.1 g of cobalt nitrate and 43.2 g of iron nitrate were added. This catalyst was composed of $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Co}_{0.5}\text{Fe}_{0.5})\text{O}_3 : (\text{Ce}_{0.65}\text{Zr}_{0.30}\text{La}_{0.05})\text{O}_2 : \text{Pd} = 50:50:0.5$ in weight ratios.

Example 6

Powder of a perovskite compound oxide

$(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ was prepared. 103.9 g of lanthanum nitrate, 26.1 g of cerium nitrate, 34.9 g of cobalt nitrate and 72.7 g of iron nitrate were dissolved in pure water, to prepare 0.3 l of an aqueous solution. Then, 0.5 l of an aqueous solution, in which 50 g of sodium carbonate was dissolved, was prepared as a neutralizer/coprecipitator. The neutralizer/coprecipitator was dripped on the aforementioned aqueous solution, to obtain a coprecipitant. This coprecipitant was sufficiently washed, filtered and then vacuum-dried. This substance was fired in the air at 600 °C for 3 hours, then pulverized, thereafter fired in the air at 800 °C for 3 hours, and further pulverized to prepare powder of $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$.

20 g of the as-obtained powder of $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ was sufficiently mixed with 80 g of the $(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2$ prepared in Example 1. This mixed powder was impregnated with palladium through an aqueous solution of palladium nitrate, dried at 110 °C for 10 hours, and fired in the air at 600 °C for 3 hours, to prepare a catalyst (sample No. 6) carrying 0.5 g of Pd.

Example 7

In place of the method of preparing the perovskite compound oxide according to Example 6, 76.7 g of lanthanum nitrate, 38.2 g of neodymium nitrate $(\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$, 43.7 g of cobalt nitrate and 60.6 g of iron nitrate were employed to prepare powder of $(\text{La}_{0.59}\text{Nd}_{0.29}\text{Ce}_{0.12})(\text{Co}_{0.5}\text{Fe}_{0.5})\text{O}_3$.

80 g of this powder was sufficiently mixed with 20 g of the $(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2$ powder prepared in Example 1, to prepare a catalyst (sample No. 7) carrying 0.5 g of Pd in a similar manner to Example 6.

Example 8

98.6 g of oxy zirconium nitrate was added to 137.70 g of the cerium oxide powder employed in Example 1, to obtain heat resistant compound oxide powder of

5 $(\text{Ce}_{0.8}\text{Zr}_{0.7})\text{O}_2$ in a similar manner to Example 1.

50 g of this heat resistant compound oxide powder was sufficiently mixed with 50 g of the perovskite powder of $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ according to Example 6, to prepare a catalyst (sample No. 8) carrying 0.5 g of Pd.

10 Example 9

80 g of the $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ powder according to Example 6 was sufficiently mixed with 20 g of heat resistant compound oxide powder of $(\text{Ce}_{0.8}\text{Zr}_{0.2})\text{O}_2$ according to Example 8, to prepare a catalyst (sample No. 9) carrying 0.5 g of Pd.

15 Example 10

In place of the cerium nitrate employed in Example 6, 12.7 g of strontium nitrate was employed to prepare perovskite powder of $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ in a similar manner thereto. 80 g of this powder was
20 sufficiently mixed with 20 g of the heat resistant compound oxide powder of $(\text{Ce}_{0.8}\text{Zr}_{0.2})\text{O}_2$ according to Example 8, to prepare a catalyst (sample No. 10) carrying 0.5 g of Pd.

Comparative Example 1

25 100 g of the perovskite compound oxide powder of $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ according to Example 6 was employed with an aqueous solution of palladium nitrate, to prepare a catalyst (sample No. C1) carrying 0.5 g of Pd according to comparative example 1 in a similar manner to Example 1.

Comparative Example 2

30 In place of the heat resistant compound oxide prepared in Example 1, 50 g of commercially available cerium oxide powder having a high specific surface area was employed to carry $(\text{La}_{0.8}\text{Ce}_{0.2})\text{CoO}_3$ on CeO_2 in a similar manner to Example 1, as well as to carry 0.5 g of Pd, thereby preparing a catalyst (sample No. C2) according to comparative example 2. This catalyst was composed of $(\text{La}_{0.8}\text{Ce}_{0.2})\text{CoO}_3:\text{CeO}_2:\text{Pd} =$
35 50:50:0.5 in weight ratios.

Comparative Example 3

40 $(\text{Ce}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.05})\text{O}_2$ of Example 1 was replaced by commercially available $\gamma\text{-Al}_2\text{O}_3$ having a specific surface area of $110\text{m}^2/\text{g}$, to prepare a catalyst (sample No. C3) according to comparative example 3 in a similar manner to the above.

Comparative Example 4

45 50 g of the perovskite compound oxide powder of $(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ prepared in Example 6 was sufficiently mixed with 50 g of commercially available SrZrO_2 powder, to prepare a catalyst (sample No. C4) carrying 0.5 g of Pd according to comparative example 4.

Test

50 Endurance tests were made on the catalysts prepared in Examples and comparative examples, in exhaust gas of an inlet gas temperature of 930°C for 5 hours, in relation to purification activity. The gas was composed of 1.0 % of carbon monoxide (CO), 0.1 % of propylene (C_3H_6), 10 % of carbon dioxide (CO_2) and 4 % of water (H_2O) under a fluctuating condition of oxygen (O_2) with a residual part of nitrogen
55 (N_2).

Evaluation

As to the catalysts which were subjected to the aforementioned endurance tests, purification factors for carbon monoxide, propylene and nitrogen oxide at 450 °C were measured. As to such measurement, the pulverulent catalysts were pressure-formed into pellets of about 2 mm in diameter, and charged into reaction tubes. The measurement was carried out at a space velocity of 30000/h., with a gas composition of 0.7 % of CO, 0.15 % of C₃H₆, 10 % of CO₂, 10 % of H₂O, 0.23 % of H₂ and 0.15 % of NO, under a fluctuating condition of O₂ with a residual part of N₂.

Table 1 shows the results and the catalytic components. It is understood from Table 1 that the catalysts according to Examples are superior in endurance to those of comparative examples.

10 Examples of Second Invention

Basic Operation A: Method of Preparing Perovskite Composite Oxide Crystal Powder

Powder of a perovskite compound oxide (La_{0.8}Ce_{0.2}) (Co_{0.4}Fe_{0.6})O₃ was prepared. 103.9 g of lanthanum nitrate, 26.1 g of cerium nitrate, 34.9 g of cobalt nitrate and 72.7 g of iron nitrate were dissolved in pure water, to prepare 0.3 l of an aqueous solution. Then, a neutralizer/coprecipitator was prepared from 0.5 l of an aqueous solution in which 50 g of sodium carbonate was dissolved. The neutralizer/coprecipitator was dripped on the above aqueous solution, to obtain a coprecipitant. This coprecipitant was sufficiently washed, filtered and thereafter vacuum-dried. This substance was fired in the air at 600 °C for 3 hours, pulverized, thereafter fired in the air at 800 °C for 3 hours, and further pulverized, to prepare powder of (La_{0.8}Ce_{0.2}) (Co_{0.4}Fe_{0.6})O₃.

Basic Operation B: Preparation of Heat Resistant Oxide

111.9 g of commercially available cerium oxide powder, having a high specific surface area with a specific surface area of 170 m²/g and purity of 99.9 % /TREO, was prepared as a heat resistant oxide for serving as a co-catalyst, and 147.9 g of an aqueous solution of oxy zirconium nitrate (ZrO(NO₃)₂), having liquid specific gravity of 1.51 and containing 25.0 percent by weight of ZrO(NO₃)₂ in ZrO₂ conversion, and 26.0 g of an aqueous solution of yttrium nitrate (Y(NO₃)₃), having liquid specific gravity of 1.62 and containing 21.7 percent by weight of Y(NO₃)₃ in Y₂O₃ conversion, were added to the heat resistant oxide, stirred and mixed with each other, and the as-formed mixture was dried in the air at 110 °C for 10 hours. Thereafter the mixture was fired in the air at 600 °C for 3 hours, to obtain about 150 g of a compound oxide of (Ce_{0.65}Zr_{0.30}Y_{0.05})O₂.

35 Basic Operation C: Slurry Coating (Carrying)

Slurry was obtained by adding 10 to 100 parts by weight, e.g., 50 parts by weight, of perovskite compound oxide crystal powder and 0 to 90 parts by weight, e.g., 50 parts by weight, of heat resistant oxide powder to 100 parts by weight of pure water and pulverizing and mixing the elements in a ball mill for 12 hours, and introduced into a cordierite ceramic monolithic substrate while an excessive part of the slurry was blown out by an air jet, dried at 130 °C for 4 hours, for example, and thereafter fired in the air at 600 °C for 3 hours, to obtain a support which was uniformly coated with the perovskite compound oxide and the heat resistant oxide.

45 Basic Operation D: Method of Carrying Pd and Solid Dissolution in Perovskite Composite Oxide Crystal

As to the coated support obtained in the basic operation C, prepared was a palladium salt solution which was weighed to be 0.2 to 5.0 parts by weight in Pd metal conversion with respect to 100 parts by weight of the perovskite compound oxide powder and the heat resistant oxide powder. The coated support was dipped in this aqueous solution or a diluted solution thereof to impregnate the total amount of Pd into the perovskite compound oxide powder and the heat resistant oxide powder. At this time, the solution was adjusted to be not more than pH 4.

Example 11

100 parts by weight of (La_{0.8}Ce_{0.2}) (Co_{0.4}Fe_{0.6})O₃ obtained by the basic operation A was uniformly coated on the inner surface of a monolithic support. 56.8 parts by weight of a palladium nitrate solution, a product by Tanaka Kikinzoku Kogyo Kabushiki Kaisha containing 4.4 percent by weight of Pd metal, which

was weighed to contain 2.5 parts by weight of palladium nitrate in Pd conversion on the basis of the basic operation D, was dissolved in 100 parts by weight of dilute nitric acid. The pH of this solution was 0.2. The total amount of this solution was impregnated into the aforementioned coated monolithic support, which in turn was dried at 130 °C for 24 hours, and fired in the air at 600 °C for 3 hours.

5

Example 12

50 parts by weight of $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ obtained by the basic operation A and 50 parts by weight of $(Ce_{0.85}Zr_{0.30}Y_{0.05})O_2$ obtained by the basic operation B were uniformly coated onto the inner surface of a monolithic support on the basis of the basic operation C. On the other hand, 25 parts by weight of a palladium nitrate solution, a product by Takana Kikinzoku Kogyo Kabusiki Kaisha containing 4.4 percent by weight of Pd metal, which was weighted to contain 1.1 parts by weight of palladium nitrate in Pd conversion on the basis of the basic operation D, was dissolved in 100 parts by weight of dilute nitric acid. The pH of this solution was 0.2. The total amount of this solution was impregnated into the aforementioned coated monolithic support, which in turn was dried at 130 °C for 24 hours, and fired in the air at 600 °C for 3 hours.

Example 13

A sample was prepared by the basic operations A, B, C and D similarly to Example 12, while a coated monolithic support which was impregnated with a palladium salt solution and dried was thereafter fired in the air at 250 °C for 3 hours.

Example 14

The basic operations A, B and C were carried out similarly to Example 12, while 25 parts by weight of a palladium nitrate solution containing 4.4 percent by weight of Pd was diluted with 1700 parts by weight of pure water in the basic operation D. The pH of this solution was 1.7. A beaker containing this solution was kept at a temperature of 40 °C in a water bath, so that a coated monolithic support formed by the basic operation C was sucked in this palladium salt solution and held for 2 hours, to adsorb palladium. Thereafter the support was dried at 130 °C for 24 hours, and thereafter fired in the air at 600 °C for 3 hours.

Example 15

A sample was prepared in a similar manner to Example 14, except for that aqueous ammonia was added to a palladium nitrate solution to adjust the pH to 3.0.

Example 16

A sample was prepared in a similar manner to Example 14, except for that aqueous ammonia was added to a palladium nitrate solution to adjust the pH to 4.0.

Example 17

50 ml of an aqueous solution, in which 22.1 g of lanthanum nitrate $(La(NO_3)_3 \cdot 6H_2O)$ was dissolved, was employed in place of 26.0 g of the yttrium nitrate solution in the basic operation B, to obtain a heat resistant compound oxide of $(Ce_{0.85}Zr_{0.30}La_{0.05})O_2$.

A sample was prepared in a similar manner to Example 12, except for that 20 parts by weight of perovskite compound oxide powder of $(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ and 80 parts by weight of the aforementioned heat resistant oxide $(Ce_{0.85}Zr_{0.30}La_{0.05})O_2$ were employed and 0.44 parts by weight of a palladium nitrate solution was employed with respect to 100 parts by weight of the oxide in Pd conversion.

Example 18

87.3 g of cobalt nitrate was employed in place of 34.9 g in the basic operation A with no employment of iron nitrate, to prepare perovskite compound oxide powder of $(La_{0.8}Ce_{0.2})CoO_3$.

In the basic operation B, 137.7 g of cerium nitrate powder and 98.6 g of an oxy zirconium nitrate solution were employed in place of 111.9 g and 147.9 g respectively with no employment of a yttrium nitrate solution, to prepare $(Ce_{0.8}Zr_{0.2})O_2$ powder.

In the basic operation C, 80 parts by weight of a perovskite compound oxide and 20 parts by weight of a heat resistant oxide were employed, to prepare a coated support.

In the basic operation D, 80 parts by weight of a palladium nitrate solution containing 4.4 percent by weight of Pd was diluted with 1700 parts by weight of pure water, to contain 3.52 parts by weight of palladium nitrate in Pd conversion. The pH of this solution was 1.1. Thereafter a sample was prepared in a similar manner to Example 13.

Example 19

20 parts by weight of the perovskite compound oxide $(La_{0.8}Ce_{0.2})CoO_3$ employed in Example 18 was employed with 80 parts by weight of commercially available CeO_2 in place of the heat resistant oxide. In the basic operation D, 40 parts by weight of a palladium nitrate solution containing 4.4 percent by weight of Pd was diluted with 1700 parts by weight of pure water to contain 1.76 parts by weight of palladium nitrate in Pd conversion. The pH of this solution was 1.4. Thereafter a sample was prepared in a similar manner to Example 17.

Example 20

An aqueous solution, in which 79.2 parts by weight of lanthanum nitrate, 8.9 parts by weight of cerium nitrate, 23.7 parts by weight of cobalt nitrate and 49.6 parts by weight of iron nitrate were dissolved, was added to 50 parts by weight of a $(Ce_{0.65}Zr_{0.30}Y_{0.05})O_3$ heat resistant compound oxide powder obtained by the basic operation B, and the mixture was dried in the air at $110^\circ C$ for 10 hours. Thereafter the mixture was fired in the air at $800^\circ C$ for 3 hours to thermally decompose the nitrate components, thereby obtaining powder in which a perovskite compound oxide $(La_{0.9}Ce_{0.1})(Co_{0.4}Fe_{0.6})O_3$ was carried on $(CeZrY)O_2$. This powder was composed of $(La_{0.9}Ce_{0.1})(Co_{0.4}Fe_{0.6})O_3$: $(Ce_{0.65}Zr_{0.30}Y_{0.05})O_3$ of 50:50 in a weight ratio.

100 parts by weight of this mixed powder was employed in the basic operation C, to prepare a coated support.

In the basic operation D, 7.66 parts by weight of a nitrate solution of dinitrodiamine platinum $((NH_3)_2(NO_2)_2Pt)$, a product of Tanaka Kikinzoku Kogyo Kabushiki Kaisha containing 4.57 percent by weight of Pt, and 25.4 parts by weight of an aqueous solution of ruthenium nitrate $(Ru(NO_3)_2)$, a product of Tanaka Kikinzoku Kogyo Kabushiki Kaisha containing 3.93 percent by weight of Ru, to contain 0.35 parts by weight of dinitrodiamine platinum in Pt conversion and 1.0 part by weight of ruthenium nitrate in Ru conversion respectively, and this mixture was diluted with 100 parts by weight of pure water. The pH of this solution was 0.5. The total amount of this solution was impregnated into the aforementioned coated monolithic support, which in turn was dried at $130^\circ C$ for 24 hours, and fired in the air at $600^\circ C$ for 3 hours.

Comparative Example a

A sample was prepared similarly to Example 14, except for that aqueous ammonia was added to a palladium nitrate solution to adjust the pH to 6.9.

Comparative Example b

A sample was prepared similarly to Example 14, except for that aqueous ammonia was added to a palladium nitrate solution to adjust the pH to 8.5.

Comparative Example c

A sample was prepared similarly to Example 14, except for that aqueous ammonia was added to a palladium nitrate solution to adjust the pH to 9.7.

Comparative Example d

12.8 g of strontium nitrate was employed in the basic operation A in place of 26.1 g of cerium nitrate, to obtain powder of a perovskite compound oxide $(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$. In the basic operation B, 50 parts by weight of the perovskite compound oxide $(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$ was employed, with 50 parts by weight of commercially available $SrZrO_3$ in place of the heat resistant oxide. Thereafter a sample was prepared in a similar manner to Example 13.

Comparative Example e

An automotive catalyst of Pt-Rh/ γ -Al₂O₃ was employed. The content of Pt-Rh was 0.43 parts by weight.

5 Comparative Example f

An automotive catalyst of Pd/ γ -Al₂O₃ was employed. The content of Pd was 1.33 parts by weight. Table 2 shows the results.

10 Measurement of Catalytic Activity

Activity levels of the respective samples supported by cordierite monolithic substrates, having cell numbers of 400/inch², of 30 mm in diameter and 50 mm in length with model gases shown in Table 3. Gas temperatures are shown by inlet gas temperatures, which were raised up from the room temperature, the temperature that concentrations of NO, CO and HC(C₃H₆ + C₃H₈) are reduced to 50 % of initial concentrations respectively is defined as a 50 % purification temperature.

Rich gases and lean gases were switched every second. The gas jets were passed through the catalysts at a space velocity (SV) of 30,000/h.

Table 3

	Rich Gas	Lean Gas
CO	2.6 %	0.7 %
HC	0.19%	0.19%
H ₂	0.87%	0.23%
CO	8 %	8 %
NO	0.17%	0.17%
O ₂	0.65%	1.8 %
H ₂ O	10 %	10 %
N ₂	Residual Part	Residual Part
(The concentration of HC is shown in C ₁ conversion)		

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Endurance Test

The aforementioned rich and lean gases were switched every 5 seconds to repeat cycles of 30 minutes at 900 °C and 30 minutes at 750 °C 15 times respectively, thereby making endurance tests. After the endurance tests, catalytic activity levels were measured in the aforementioned method.

Table 4 shows the results of measurement of catalytic activity levels before and after the endurance tests. As to Example 12 and comparative example e, Fig. 1 shows the results of three way purification activity levels at respective temperatures.

As clearly understood from Table 4, Examples of the present invention exhibited low 50 % purification temperatures, while comparative examples exhibited high values. It is conceivable that recrystallization of the perovskite compound oxide incorporating metallic salts eluded on the surface of the perovskite compound oxide serving as a core and impregnated and/or adsorbed Pd salts was insufficient due to the low firing temperature in Example 12, while this sample was exposed to a high temperature during the endurance test, to form a perovskite compound oxide crystal in which Pd was solidly dissolved, thereby forming a double structure similarly to other Examples.

Through the aforementioned observation, it is conceivable that the inventive catalysts were in double structures formed by cores of oxides containing no precious metals and outer layers of perovskite compound oxides in which precious metals were solidly dissolved.

Figs. 2 to 4 are photographs of Example 14 observed with a scanning electron microscope (SEM). The magnifications are successively increased along Figs. 2 to 4. According to these photographs, it is observed that fine particles of a perovskite compound oxide, which may have been eluded and recrystallized, enclose particles of a perovskite compound oxide (LaCe) (FeCo)O₃ of 25 to 30 μ m. The fine particles also partially enclose particles of a heat resistant oxide (CeZrY)O₂ of 3 to 5 μ m.

X-Ray Diffraction Analysis

Only the catalytic layer was scraped off from the sample of Example 12 before the endurance test to collect powder, which in turn was subjected to material identification through X-ray diffraction. From its peak profile, it was observed that LaFeO perovskite phases (JCPDS card 37-1493) and CeO phases (JCPDS card 34-0394) were dominant with a slight amount of Pd phases (JCPDS card 5-0681). No other phases were observed, and it was confirmed that the composition eluded in carrying of Pd again formed perovskite phases by firing.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

The features disclosed in the foregoing description, in the claims and/or in the accompanying drawings may, both, separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

Table 1

No.	Composition of Catalyst (Weight ratio)		Purification Factor			
	Perovskite Compound Oxide	Heat Resistant Oxide	Precious Metal	CO	C ₃ H ₆	NO
1	[50]La _{0.8} Ce _{0.2} CoO ₃	[50](CeZrY)O ₂	[0.5]Pd	85	83	85
2	[50]La _{0.8} Ce _{0.2} Co _{0.4} Fe _{0.6} O ₃	[50](CeZrY)O ₂	[0.5]Pd	93	86	92
3	[50]La _{0.8} Ce _{0.2} Co _{0.4} Fe _{0.6} O ₃	[50](CeZrY)O ₂	[0.5]Pd	91	85	86
4	[50]La _{0.9} Ce _{0.1} Co _{0.4} Fe _{0.6} O ₃	[50](CeZrY)O ₂	[0.5]Pt	89	81	80
5	[50]La _{0.8} Sr _{0.2} Co _{0.5} Fe _{0.5} O ₃	[50](CeZrLa)O ₂	[0.5]Pd	93	85	87
6	[20]La _{0.8} Ce _{0.2} Co _{0.4} Fe _{0.6} O ₃	[80](CeZrY)O ₂	[0.5]Pd	86	84	84
7	[80]La _{0.59} Nd _{0.29} Ce _{0.12} Co _{0.5} Fe _{0.5} O ₃	[20](CeZrY)O ₂	[0.5]Pd	87	84	85
8	[50]La _{0.8} Ce _{0.2} Co _{0.4} Fe _{0.6} O ₃	[50](CeZr)O ₂	[0.5]Pd	85	82	83
9	[80]La _{0.8} Ce _{0.2} Co _{0.4} Fe _{0.6} O ₃	[20](CeZr)O ₂	[0.5]Pd	88	80	87
10	[80]La _{0.8} Sr _{0.2} Co _{0.4} Fe _{0.6} O ₃	[20](CeZr)O ₂	[0.5]Pd	86	80	85
C1	[100]La _{0.8} Ce _{0.2} Co _{0.4} Fe _{0.6} O ₃	-----	[0.5]Pd	82	70	68
C2	[50]La _{0.8} Ce _{0.2} CoO ₃	[50]CeO ₂	[0.5]Pd	73	68	61
C3	[50]La _{0.8} Ce _{0.2} CoO ₃	[50]γ-Al ₂ O ₃	[0.5]Pd	61	57	55
C4	[50]La _{0.8} Ce _{0.2} Co _{0.4} Fe _{0.6}	[50]SrZrO ₃	[0.5]Pd	85	80	80

Table 2

No	Starting System [Weight ratio]			Soln. pH	Firing
	Perovskite Compound Oxide	Heat Resistant Oxide	Precious Metal		
11	[100](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃		[2.5]Pd	0.2	600 ° C
12	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	0.2	600 ° C
13	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	0.2	250 ° C
14	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	1.7	600 ° C
15	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	3.0	600 ° C
16	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	4.0	600 ° C
17	[20](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[80](Ce _{0.65} Zr _{0.3} La _{0.05})O ₂	[0.44] Pd	0.2	600 ° C
18	[80](La _{0.8} Ce _{0.2})CoO ₃	[20](Ce _{0.8} Zr _{0.2})O ₂	[3.52] Pd	1.1	600 ° C
19	[20](La _{0.8} Ce _{0.2})CoO ₃	[80]CeO ₂	[1.76] Pd	1.4	600 ° C
20	[50](La _{0.8} Ce _{0.1})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[0.3]Pt [1.0]Ru	0.5	600 ° C
a	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	6.9	600 ° C
b	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	8.5	600 ° C
c	[50](La _{0.8} Ce _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05})O ₂	[1.1]Pd	9.7	600 ° C
d	[50](La _{0.8} Sr _{0.2})(Co _{0.4} Fe _{0.6})O ₃	[50]SrZrO ₃	[1.1]Pd	1.7	600 ° C
e		[100]γ-Al ₂ O ₃	[0.43] Pt-Rh	1.8	250 ° C
f		[100]γ-Al ₂ O ₃	[1.13] Pd	1.4	250 ° C

Table 4.

50 % Purification Temperature (°C)

No.	Initial Temperature			After Endurance Test		
	NO	CO	HC	NO	CO	HC
Example						
1 1	1 1 9	1 1 7	1 2 2	2 1 2	2 4 1	2 3 9
1 2	1 2 1	1 1 3	1 2 3	1 9 8	1 9 2	2 0 7
1 3	1 4 1	1 4 0	1 5 5	2 0 5	2 2 2	2 2 5
1 4	1 2 5	1 1 9	1 3 7	2 0 5	2 1 5	2 2 9
1 5	1 6 8	1 6 8	1 7 2	2 4 8	2 6 4	2 6 4
1 6	2 0 0	1 9 9	2 0 6	2 7 1	2 7 6	2 7 6
1 7	1 8 7	1 7 6	1 7 8	2 6 1	2 5 7	2 6 5
1 8	1 2 1	1 1 1	1 3 2	2 1 2	1 9 5	2 2 5
1 9	1 4 5	1 3 5	1 4 8	2 3 7	2 1 4	2 3 7
2 0	1 5 7	1 5 5	1 5 7	2 0 8	2 4 3	2 4 2
Comparative Example						
a	2 3 6	2 2 7	2 4 2	3 7 0	3 3 2	3 4 9
b	2 5 3	2 4 5	2 5 6	3 7 4	2 8 8	3 3 2
c	2 3 3	2 2 5	2 3 6	4 3 2	3 6 5	3 8 2
d	3 1 7	3 0 6	3 4 1	> 5 0 0	3 9 4	3 9 3
e	1 9 8	1 9 3	2 0 8	2 5 9	2 6 3	2 7 6
f	1 7 5	1 8 5	1 8 6	3 0 1	3 1 8	3 1 3

50 Claims

1. An exhaust gas purifying catalyst comprising:

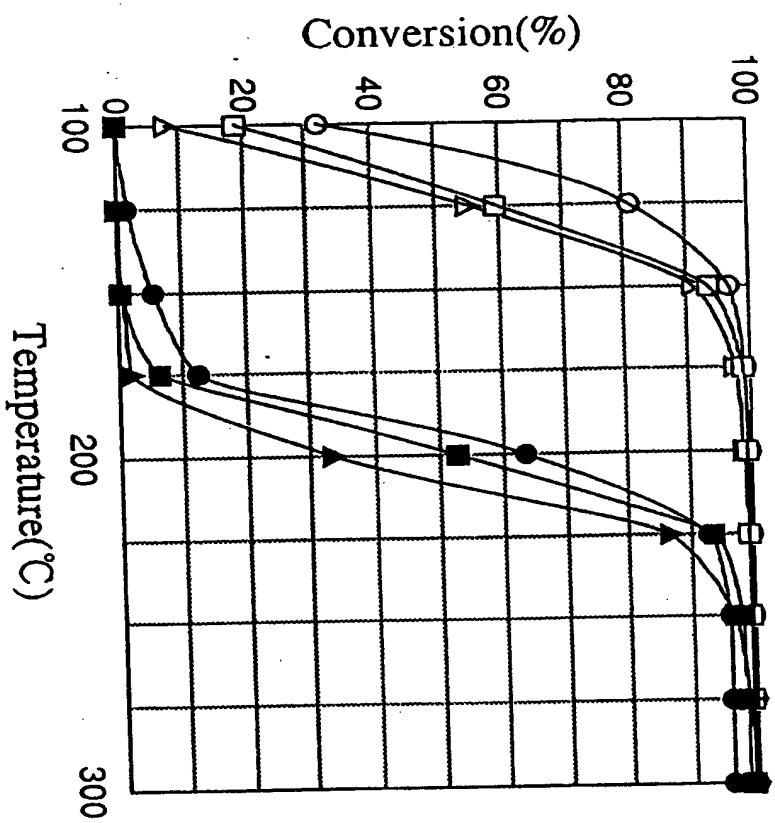
a perovskite compound oxide being expressed by a general formula $\text{Ln}_{1-x}\text{AxMO}_3$, where Ln represents at least one rare earth metal excluding Ce, A represents Ce or at least one alkaline earth metal, M represents at least one transition metal and $0 < x < 1$;

a heat resistant oxide containing Ce and Zr, with or without at least one rare earth metal excluding Ce, said heat resistant oxide being at least partially in the form of a compound oxide or a solid solution; and

at least one precious metal.

2. An exhaust gas purifying catalyst in accordance with claim 1, wherein said heat resistant oxide includes 5 to 100 atoms of said Zr and 0 to 100 atoms of said rare earth metal excluding Ce per 100 atoms of said Ce.
3. An exhaust gas purifying catalyst in accordance with claim 1, wherein said precious metal is selected from the platinum group.
4. An exhaust gas purifying catalyst at least having an oxide comprising:
 - a core of a perovskite compound oxide being expressed by a general formula $\text{Ln}_1\text{-xBxMO}_3$, where Ln represents at least one rare earth metal excluding Ce, B represents Ce or at least one alkaline earth metal excluding Sr, M represents at least two transition metal and $0 < x < 1$; and
 - an outer perovskite compound oxide being formed around said core and having a precious metal solidly dissolved therein.
5. An exhaust gas purifying catalyst in accordance with claim 4, further comprising a heat resistant oxide of Ce, or a heat resistant oxide containing Ce and Zr, or further containing at least one rare earth metal excluding Ce, said heat resistant oxide being at least partially in the form of a compound oxide and/or a solid solution.
6. An exhaust gas purifying catalyst in accordance with claim 5, wherein said heat resistant oxide containing Ce and Zr includes 5 to 100 atoms of said Zr and 0 to 100 atoms of said rare earth metal excluding Ce per 100 atoms of Ce.
7. An exhaust gas purifying catalyst in accordance with any of claims 4, 5 and 6, wherein said precious metal or an oxide of said precious metal is dispersed in a fine particle state.
8. An exhaust gas purifying catalyst in accordance with any of claims 4, 5, 6 and 7, wherein said precious metal is selected from the platinum group.
9. An exhaust gas purifying catalyst in accordance with claim 8, wherein said precious metal is Pd.
10. A method of preparing an exhaust gas purifying catalyst, comprising the steps of:
 - preparing a substance consisting of a perovskite compound oxide, being expressed by a general formula $\text{Ln}_1\text{-xBxMO}_3$, where Ln represents at least one rare earth metal excluding Ce, B represents Ce or at least one alkaline earth metal excluding Sr, M represents at least one transition metal and $0 < x < 1$, or a mixture of said perovskite compound oxide and a heat resistant oxide;
 - impregnating and/or adsorbing a precious metal into said substance through a precious metal salt solution containing 0.2 to 5.0 parts by weight of a precious metal in precious metal conversion based on 100 parts by weight of said substance and being adjusted to be not more than pH 4;
 - drying said treated substance; and
 - firing said treated substance at a temperature of 250 to 800 °C.

Fig. 1
Three-way Conversion Activity of
Example 12 and Comparative Example e



- Δ Example 12 (HC)
- Example 12 (CO)
- Example 12 (NOx)
- ▲ Comparative Example e (HC)
- Comparative Example e (CO)
- Comparative Example e (NOx)

Fig.2

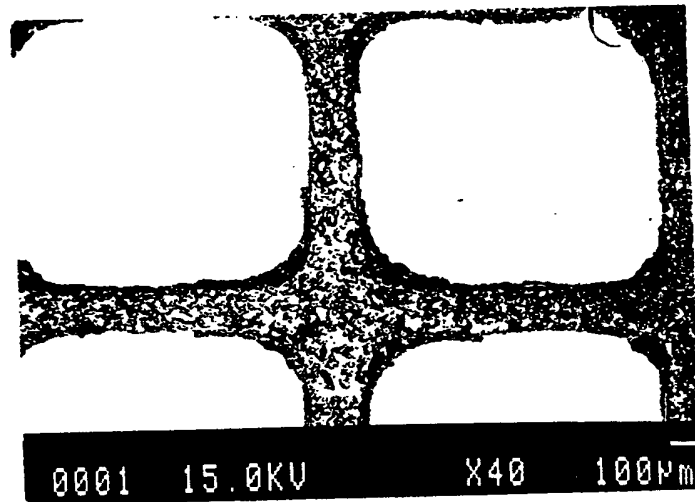


Fig.3

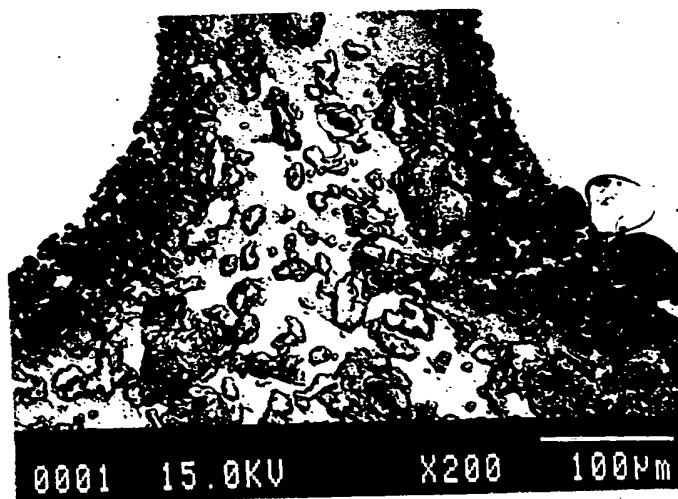
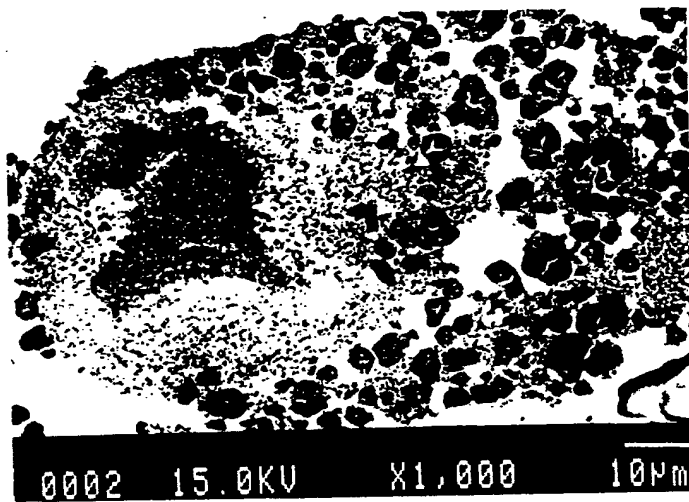


Fig. 4





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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 2717

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
D,A	US-A-4 921 829 (OZAWA ET AL.) * claims 1-9 *	1,3,8,9,10	B01D53/36 B01J23/89 B01J23/00
A	FR-A-2 343 505 (JOHNSON, MATTHEY & CO.) * claims 1-4,11,15,19 *	1,3-5,7-10	
A	FR-A-2 174 180 (HITACHI LTD.) * claims 1,11,12 *	1,10	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			B01D B01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 OCTOBER 1992	Examiner CUBAS ALCARAZ J.L.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
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